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<b>Date of Application:</b>	<b>February 21, 2002</b>
<b>Application Number:</b>	<b>Patent Application No. 2002-044362</b>
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Name of Document]	PATENT APPLICATION
[Reference Number]	IP1202
[Filing Date]	February 21, 2002
[Attention]	Commissioner of Patent Office
[International Patent Classification]	C08F 10/08
[Title of Invention]	PROCESS FOR PRODUCING HIGH-FLUIDITY 1-BUTENE-BASED POLYMER AND THE HIGH-FLUIDITY 1-BUTENE-BASED POLYMER
[Number of Claims]	7
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[Application Elements]

[Name] Specification 1

[Name] Abstract 1

[General Power of Attorney Number] 0000936

[Name of Document] SPECIFICATION

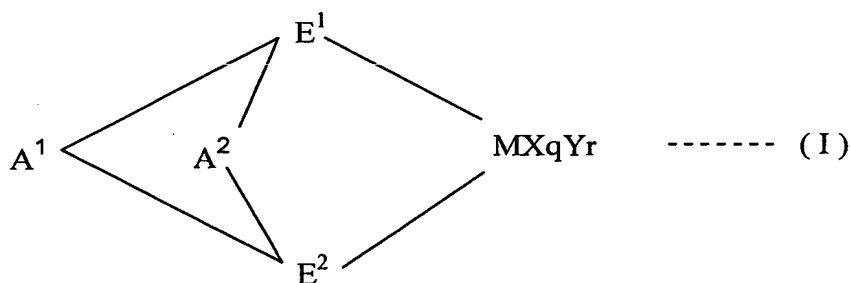
[Title of the Invention] PROCESS FOR PRODUCING  
HIGH-FLUIDITY 1-BUTENE-BASED POLYMER AND THE  
HIGH-FLUIDITY 1-BUTENE-BASED POLYMER

[Claims]

1. A process for producing a high-fluidity 1-butene-based polymer, which comprises homopolymerizing 1-butene in the presence of a polymerization catalyst comprising

(A) a transition metal compound represented by the following general formula (I):

[Chemical Formula 1]



wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$E^1$  and  $E^2$  are independently a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group, phosphide group, hydrocarbon groups and silicon-containing groups, which form a cross-linked structure via  $A^1$  and  $A^2$  and may be same or different from each other;

X is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X groups are present, these X groups may be same or different from

each other, and may be cross-linked with the other X group, E<sup>1</sup>, E<sup>2</sup> or Y;

Y is a Lewis base, and when a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group, E<sup>1</sup>, E<sup>2</sup> or X;

A<sup>1</sup> and A<sup>2</sup> are divalent cross-linking groups capable of bonding the two ligands E<sup>1</sup> and E<sup>2</sup> to each other which may be same or different from each other, and are independently a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms;

q is an integer of 1 to 5 given by the formula:

[(valence of M) - 2]; and

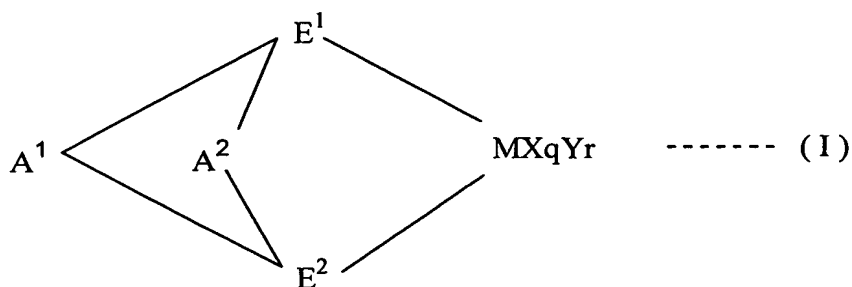
r is an integer of 0 to 3, and

(B) an organoboron compound,

thereby obtaining a high-fluidity 1-butene-based homopolymer .

2. A process for producing a high-fluidity 1-butene-based polymer, which comprises copolymerizing 1-butene with ethylene and/or an  $\alpha$ -olefin having 3 to 20 carbon atoms except for 1-butene, in the presence of a polymerization catalyst comprising  
(A) a transition metal compound represented by the following general formula (I):

[Chemical Formula 2]



wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$E^1$  and  $E^2$  are independently a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group, phosphide group, hydrocarbon groups and silicon-containing groups, which form a cross-linked structure via  $A^1$  and  $A^2$  and may be same or different from each other;

X is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X groups are present, these X groups may be same or different from each other, and may be cross-linked with the other X group,  $E^1$ ,  $E^2$  or Y;

Y is a Lewis base, and when a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group,  $E^1$ ,  $E^2$  or X;

$A^1$  and  $A^2$  are divalent cross-linking groups capable of bonding the two ligands  $E^1$  and  $E^2$  to each other which may be same or different from each other, and are independently a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group,  $-O-$ ,  $-CO-$ ,  $-S-$ ,

-SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, and they may be same or different from each other;

q is an integer of 1 to 5 given by the formula:

[(valence of M) - 2]; and

r is an integer of 0 to 3, and

(B) an organoboron compound,

thereby obtaining a high-fluidity 1-butene-based copolymer.

3. A high-fluidity 1-butene-based polymer satisfying the following requirements (1), (2) and (3):

(1) an intrinsic viscosity  $[\eta]$  measured in a tetralin solvent at 135°C is 0.01 to 0.5 dL/g;

(2) a crystalline resin having a melting point (T<sub>m</sub> - D), defined as a top of a peak observed on a highest-temperature side in a melting endothermic curve obtained by a differential scanning calorimeter (DSC) when a sample is held in a nitrogen atmosphere at -10°C for 5 min and then heated at a temperature rise rate of 10°C/min, is 0 to 100°C; and

(3) a stereoregularity index  $\{(mmmm)/(mmrr + rmmr)\}$  is 30 or lower.

4. The high-fluidity 1-butene-based polymer according to claim 3, wherein said polymer further satisfies the following requirements (4) and (5):

(4) a molecular weight distribution ( $M_w/M_n$ ) measured by gel permeation chromatography (GPC) is 4 or lower; and

(5) a weight-average molecular weight ( $M_w$ ) measured by GPC is 10,000 to 100,000.

5. A high-fluidity 1-butene-based polymer as claimed in claim 3 or 4, produced according to the process of Claim 1.

6. A high-fluidity 1-butene-based polymer as claimed in claim 3 or 4, produced according to the process of claim 2.

7. A 1-butene-based resin modifier comprising the high-fluidity 1-butene-based polymer as claimed in any one of claims 3 to 6.

#### [Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a process for producing a high fluidity 1-butene-based polymer, the 1-butene-based polymer, and a resin modifier comprising the 1-butene-based polymer. The 1-butene-based polymer according to the present invention is suitably used in various applications such as hot-melt adhesives, sealing agents, modifiers for resins and elastomers, wax blending agents and filler blending agents.

[0002]

[Prior Art]



Heretofore, as polymers that have relatively low molecular weight and crystallinity and are usable as hot-melt adhesives, etc., known are propylene homopolymers or olefin-based polymers produced by copolymerizing propylene with ethylene or 1-butene. However, these polymers are insufficient in uniformity due to broad molecular weight distribution and broad composition distribution thereof.

Meanwhile, conventionally, 1-butene polymers have been produced using magnesium-supported titanium catalysts (Japanese Patent Application Laid-Open No. Hei-7-145205(1995)). However, the thus produced 1-butene polymers have a non-uniform composition which, therefore, gives adverse influences on properties thereof such as an occurrence of stickiness and a poor transparency.

In this regard, in recent years, 1-butene polymers having a uniform composition have been produced using metallocene catalysts (Japanese Patent Application Laid-Open Nos. Sho-62-119214 (1987), Sho-62-121708 (1987), Sho-62-121707 (1987), Sho-62-119213 (1987) and Hei-8-225605 (1996)).

In addition, Japanese Patent Application Laid-Open No. Sho-63-57615 (1988) discloses high-fluidity 1-butene-based polymers. However, in any of these conventional methods, since non-crosslinked metallocene catalysts are used therein, the obtained polymers are liquid amorphous 1-butene-based polymers. Therefore, these 1-butene-based polymers have problems concerning poor surface properties, etc.

[0003]

[Problems to be Overcome by the Invention]

The present invention has been completed in view of the above circumstances. An object of the present invention is to provide a process for producing a 1-butene-based polymer having a uniform composition, a well-controlled stereoregularity, a high fluidity and a high flexibility.

[0004]

[Means to Overcome the Problem]

As a result of extensive researches for accomplishing the above objects, the inventors have found that the 1-butene-based polymers can be produced at a high activity in the presence of a polymerization catalyst composed of (A) a specific transition metal compound and (B) an organoboron compound as compared with using aluminoxane as (B) component and the obtained 1-butene-based polymers exhibit a suitable molecular weight distribution and composition distribution and also a good balance between fluidity, physical property (elastic modulus) and fabricability (melting point).

The present invention has been accomplished based on the above findings.

Thus, the present invention provides the following 1-butene-based polymer, process for producing the 1-butene-based polymer, resin modifier made of the 1-butene-based polymer.

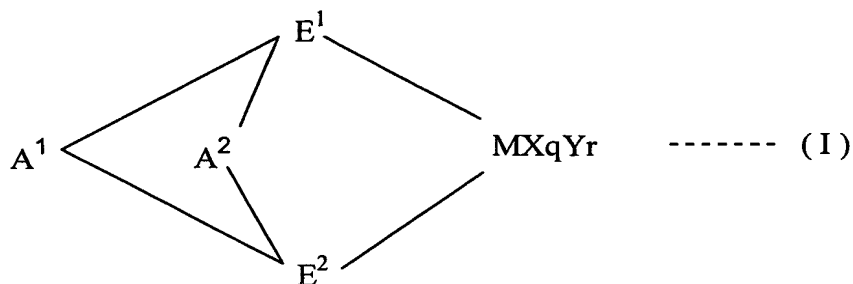
[0005]

1. A process for producing a high-fluidity 1-butene-based polymer, which comprises homopolymerizing 1-butene in the presence of a polymerization catalyst comprising  
(A) a transition metal compound represented by the following general

formula (I):

[0006]

[Chemical Formula 3]



[0007]

wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$E^1$  and  $E^2$  are independently a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group, phosphide group, hydrocarbon groups and silicon-containing groups, which form a cross-linked structure via  $A^1$  and  $A^2$  and may be same or different from each other;

X is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X groups are present, these X groups may be same or different from each other, and may be cross-linked with the other X group,  $E^1$ ,  $E^2$  or Y;

Y is a Lewis base, and when a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group,  $E^1$ ,  $E^2$  or X;

$A^1$  and  $A^2$  are divalent cross-linking groups capable of bonding the two ligands  $E^1$  and  $E^2$  to each other which may be same or different from each other, and are independently a hydrocarbon group having 1



wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$E^1$  and  $E^2$  are independently a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group, phosphide group, hydrocarbon groups and silicon-containing groups, which form a cross-linked structure via  $A^1$  and  $A^2$  and may be same or different from each other;

X is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X groups are present, these X groups may be same or different from each other, and may be cross-linked with the other X group,  $E^1$ ,  $E^2$  or Y;

Y is a Lewis base, and when a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group,  $E^1$ ,  $E^2$  or X;

$A^1$  and  $A^2$  are divalent cross-linking groups capable of bonding the two ligands  $E^1$  and  $E^2$  to each other which may be same or different from each other, and are independently a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, and they may be same or different from each other;

q is an integer of 1 to 5 given by the formula:

$[(\text{valence of M}) - 2]$ ; and

r is an integer of 0 to 3, and

(B) an organoboron compound,

thereby obtaining a high-fluidity 1-butene-based copolymer,.

3. A high-fluidity 1-butene-based polymer satisfying the following requirements (1), (2) and (3):

(1) an intrinsic viscosity  $[\eta]$  measured in a tetralin solvent at 135°C is 0.01 to 0.5 dL/g;

(2) a crystalline resin having a melting point ( $T_m - D$ ), defined as a top of a peak observed on a highest-temperature side in a melting endothermic curve obtained by a differential scanning calorimeter (DSC) when a sample is held in a nitrogen atmosphere at  $-10^\circ\text{C}$  for 5 min and then heated at a temperature rise rate of  $10^\circ\text{C}/\text{min}$ , is 0 to  $100^\circ\text{C}$ ; and

(3) a stereoregularity index  $\{(\text{mmmm})/(\text{mmrr} + \text{rmmr})\}$  is 30 or lower.

4. The high-fluidity 1-butene-based polymer as described in the above 3, wherein said polymer further satisfies the following requirements (4) and (5):

(4) a molecular weight distribution ( $M_w/M_n$ ) measured by gel permeation chromatography (GPC) is 4 or lower; and

(5) a weight-average molecular weight ( $M_w$ ) measured by GPC is 10,000 to 100,000.

5. The high-fluidity 1-butene-based polymer as described in the above 3 or 4, produced according to the process of the above 1.

6. The high-fluidity 1-butene-based polymer as described in the above 3 or 4, produced according to the process of the above 2.

7. A 1-butene-based resin modifier comprising the high-fluidity 1-butene-based polymer as described in any one of the above 3 to 6.

[0010]

[Embodiment of the Invention]

In the following descriptions, [1] the process for producing a 1-butene-based polymer, [2] the 1-butene-based polymer, and [3] the 1-butene-based resin modifier are explained in detail.

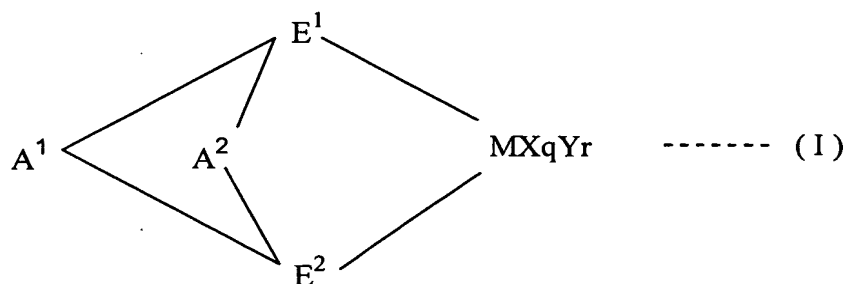
[1] Process for Production of 1-Butene-Based Polymer

In the process for production of the 1-butene-based polymer according to the present invention, the 1-butene-based polymer is produced by homopolymerizing 1-butene, or copolymerizing 1-butene with ethylene and/or an  $\alpha$ -olefin having 3 to 20 carbon atoms except for 1-butene, in the presence of a polymerization catalyst comprising:

(A) a transition metal compound represented by the following general formula (I):

[0011]

[Chemical Formula 5]



[0012]

wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$\text{E}^1$  and  $\text{E}^2$  are independently a ligand selected from the group

consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group, phosphide group, hydrocarbon groups and silicon-containing groups, which form a cross-linked structure via  $A^1$  and  $A^2$  and may be same or different from each other;

X is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X groups are present, these X groups may be same or different from each other, and may be cross-linked with the other X group,  $E^1$ ,  $E^2$  or Y;

Y is a Lewis base and when a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group,  $E^1$ ,  $E^2$  or X;

$A^1$  and  $A^2$  are divalent cross-linking groups capable of bonding the two ligands  $E^1$  and  $E^2$  to each other which may be same or different from each other, and are independently a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group,  $-O-$ ,  $-CO-$ ,  $-S-$ ,  $-SO_2-$ ,  $-Se-$ ,  $-NR^1-$ ,  $-PR^1-$ ,  $-P(O)R^1-$ ,  $-BR^1-$  or  $-AlR^1-$  wherein  $R^1$  is a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms;

q is an integer of 1 to 5 given by the formula:

$[(\text{valence of } M) - 2]$ ; and

r is an integer of 0 to 3, and

(B) an organoboron compound.

[0013]



In the above general formula (I), M represents a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table. Specific examples of the metal element M include titanium, zirconium, hafnium, yttrium, vanadium, chromium, manganese, nickel, cobalt, palladium and lanthanoid metals. Of these metal elements, preferred are titanium, zirconium and hafnium from the standpoint of a good catalytic activity for polymerization of olefins.

E<sup>1</sup> and E<sup>2</sup> are independently a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide group ( $\cdot\text{N}<$ ), phosphide group ( $\cdot\text{P}<$ ), hydrocarbon groups ( $>\text{CR}\cdot$ ,  $>\text{C}<$ ) and silicon-containing groups ( $>\text{SiR}\cdot$ ,  $>\text{Si}<$ ) wherein R is hydrogen, a hydrocarbon group having 1 to 20 carbon atoms or a hetero atom-containing group, and form a cross-linked structure via A<sup>1</sup> and A<sup>2</sup>.

The ligands E<sup>1</sup> and E<sup>2</sup> may be same or different from each other.

Of these ligands E<sup>1</sup> and E<sup>2</sup>, preferred are substituted cyclopentadienyl, indenyl and substituted indenyl.

[0014]

X represents a ligand capable of forming a  $\sigma$ -bond. When a plurality of X groups are present, these X groups may be same or different from each other, and may be cross-linked with the other X group, E<sup>1</sup>, E<sup>2</sup> or Y.

Specific examples of the ligand X include a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an aryloxy group having 6 to 20 carbon

atoms, an amide group having 1 to 20 carbon atoms, a silicon-containing group having 1 to 20 carbon atoms, a phosphide group having 1 to 20 carbon atoms, a sulfide group having 1 to 20 carbon atoms, and an acyl group having 1 to 20 carbon atoms.

Y represents a Lewis base. When a plurality of Y groups are present, these Y groups may be same or different from each other, and may be cross-linked with the other Y group, E<sup>1</sup>, E<sup>2</sup> or X.

Specific examples of the Lewis base as Y include amines, ethers, phosphines and thioethers.

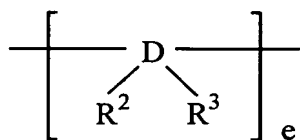
[0015]

A<sup>1</sup> and A<sup>2</sup> are divalent cross-linking groups capable of bonding the two ligands to each other which may be same or different from each other, and are independently represent a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms, or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms.

The cross-linking groups include, for example, groups represented by the following general formula:

[0016]

[Chemical Formula 6]



[0017]

wherein D is carbon, silicon or tin; R<sup>2</sup> and R<sup>3</sup> are independently a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, and may be same or different from each other and may be bonded to each other to form a ring; and e is an integer of 1 to 4. Specific examples of the cross-linking groups represented by the above formula include methylene, ethylene, ethylidene, propylidene, isopropylidene, cyclohexylidene, 1,2-cyclohexylene, vinylidene (CH<sub>2</sub>=C=), dimethylsilylene, diphenylsilylene, methylphenylsilylene, dimethylgermylene, dimethylstannylene, tetramethyldisilylene and diphenyldisilylene.

Of these cross-linking groups, preferred are ethylene, isopropylidene and dimethylsilylene. The symbol q is an integer of 1 to 5 given by the formula:

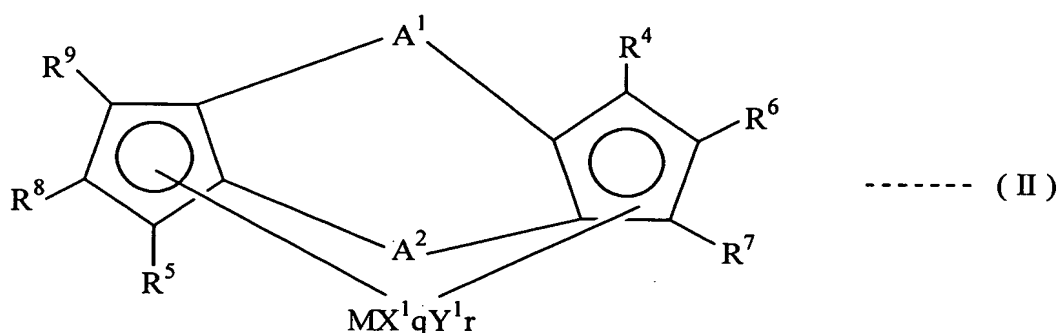
[(valence of M) - 2], and

r is an integer of 0 to 3.

Of these transition metal compounds represented by the above general formula (I), preferred are transition metal compounds having as a ligand, a double crosslinking type biscyclopentadienyl derivative represented by the following general formula (II):

[0018]

[Chemical Formula 7]



[0019]

In the above general formula (II), M, A<sup>1</sup>, A<sup>2</sup>, q and r have the same definitions as described previously.

X<sup>1</sup> is a ligand capable of forming a  $\sigma$ -bond, and when a plurality of X<sup>1</sup> groups are present, these X<sup>1</sup> groups may be same or different from each other and may be cross-linked with the other X<sup>1</sup> group or Y<sup>1</sup>.

Specific examples of the X<sup>1</sup> groups are the same as exemplified above with respect to X of the general formula (I).

Y<sup>1</sup> is a Lewis base, and when a plurality of Y<sup>1</sup> groups are present, these Y<sup>1</sup> groups may be same or different and may be cross-linked with the other Y<sup>1</sup> group or X<sup>1</sup>.

Specific examples of the Y<sup>1</sup> groups are the same as exemplified above with respect to Y of the general formula (I).

R<sup>4</sup> to R<sup>9</sup> are independently a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group or a hetero atom-containing group. However, at least one of R<sup>4</sup> to R<sup>9</sup> should be a group other than a hydrogen atom.

Also, R<sup>4</sup> to R<sup>9</sup> may be same or different from each other, and adjacent two groups thereof may be bonded to each other to form a ring.

In particular, R<sup>6</sup> and R<sup>7</sup> are preferably bonded to form a ring, and also R<sup>8</sup> and R<sup>9</sup> are preferably bonded to each other to form a ring.

R<sup>4</sup> and R<sup>5</sup> are preferably groups containing a hetero atom such as oxygen, halogen and silicon, because these groups exhibit a high polymerization activity.

[0020]

The transition metal compound containing double crosslinking type biscyclopentadienyl derivatives as ligands preferably contains silicon in the crosslinking group between the ligands.

Specific examples of the transition metal compounds represented by the general formula (I) include

(1,2'-ethylene)(2,1'-ethylene)-bis(indenyl)zirconium dichloride,

(1,2'-methylene)(2,1'-methylene)-bis(indenyl)zirconium dichloride,

(1,2'-isopropylidene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(3-methylindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(4,5-benzindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(4-isopropylindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(5,6-dimethylindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(4,7-diisopropylindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(4-phenylindenyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(3-methyl-4-isopropylindenyl)-

zirconium dichloride,

(1,2'-ethylene)(2,1'-ethylene)-bis(5,6-benzoindenyl)zirconium  
dichloride,

(1,2'-ethylene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride,

(1,2'-methylene)(2,1'-ethylene)-bis(indenyl)zirconium dichloride,

(1,2'-methylene)(2,1'-isopropylidene)-bis(indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(indenyl)zirconium  
dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-methylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-n-butylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-i-propylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilyl-  
methylindenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-phenylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(4,5-benzoindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(4-isopropylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(5,6-dimethylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(4,7-di-i-propyl-  
indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(4-phenylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-methyl-4-i-propyl-  
indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(5,6-benzoindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(indenyl)zirconium  
dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-methylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-i-propylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-n-butylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-trimethylsilylmethyl-  
indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-trimethylsilyl-  
indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)-bis(3-phenylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(indenyl)zirconium  
dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(3-methylindenyl)zirconium  
dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(3-i-propylindenyl)zirconium  
dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(3-n-butylinde-  
nyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(3-trimethylsilylmethyl-  
indenyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-methylene)-bis(3-trimethylsilylindenyl)-  
zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(indenyl)zirconium  
dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(3-methylindenyl)zirconium  
dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(3-i-propylindenyl)zirconium  
dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(3-n-butylinde-  
nyl)zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(3-trimethylsilylmethyl-  
indenyl)zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-methylene)-bis(3-trimethylsilylindenyl)-  
zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methylcyclo-  
pentadienyl) (3'-methylcyclopentadienyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)  
(3'-methylcyclopentadienyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-ethylene)(3-methylcyclopentadienyl)  
(3'-methylcyclopentadienyl)zirconium dichloride,

(1,2'-ethylene)(2,1'-methylene)(3-methylcyclopentadienyl)  
(3'-methylcyclopentadienyl)zirconium dichloride,



(1,2'-ethylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)  
 (3'-methylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-methylene)(3-methylcyclopentadienyl)  
 (3'-methylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)  
 (3'-methylcyclopentadienyl)zirconium dichloride,  
 (1,2'-isopropylidene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)  
 (3'-methylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3,4-dimethylcyclo-  
 pentadienyl) (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3,4-dimethylcyclo-  
 pentadienyl) (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3,4-dimethylcyclopentadienyl)  
 (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-methylene)(3,4-dimethylcyclopentadienyl)  
 (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)  
 (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-methylene)(3,4-dimethylcyclopentadienyl)  
 (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)  
 (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-isopropylidene)(2,1'-isopropylidene)(3,4-dimethylcyclo-  
 pentadienyl) (3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-ethylcyclo-  
 pentadienyl) (3'-methyl-5'-ethylcyclopentadienyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-ethylcyclopentadienyl) (3'-methyl-5'-ethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-isopropylcyclopentadienyl) (3'-methyl-5'-isopropylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-n-butylcyclopentadienyl) (3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-phenylcyclopentadienyl) (3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-ethylcyclopentadienyl) (3'-methyl-5'-ethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopentadienyl) (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-n-butylcyclopentadienyl) (3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-phenylcyclopentadienyl) (3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-ethylcyclopentadienyl) (3'-methyl-5'-ethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-i-propylcyclopentadienyl) (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-n-butylcyclopentadienyl) (3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-phenylcyclopenta-  
 dienyl) (3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-ethylcyclopenta-  
 dienyl) (3'-methyl-5'-ethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentad-  
 ienyl) (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-n-butylcyclopenta-  
 dienyl) (3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-phenylcyclopenta-  
 dienyl) (3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentadienyl)  
 (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopenta-  
 dienyl) (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentadienyl)  
 (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopenta-  
 dienyl) (3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)bisindenyl zirconium  
 dichloride,  
 (1,1'-diphenylsilylene)(2,2'-dimethylsilylene)bisindenyl zirconium  
 dichloride,  
 (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)bisindenyl zirconium  
 dichloride,  
 (1,1'-diisopropylsilylene)(2,2'-dimethylsilylene)bisindenyl zirconium  
 dichloride,

(1,1'-dimethylsilylene)(2,2'-diisopropylsilylene)bisindenyl zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-diphenylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-diphenylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-diisopropylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-diisopropylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-diisopropylsilylene)(2,1'-diisopropylsilylene) (indenyl)

(3-trimethylsilylindenyl) zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylmethylindenyl) zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-diphenylsilylene) (indenyl)

(3-trimethylsilylmethylindenyl) zirconium dichloride,

(1,2'-diphenylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylmethylindenyl) zirconium dichloride,

(1,2'-dimethylsilylene)(2,1'-diphenylsilylene) (indenyl)

(3-trimethylsilylmethylindenyl) zirconium dichloride,

(1,2'-diisopropylsilylene)(2,1'-dimethylsilylene) (indenyl)

(3-trimethylsilylmethylindenyl) zirconium dichloride,

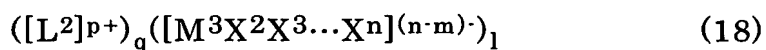
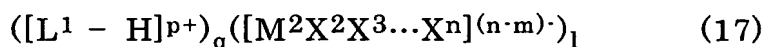
(1,2'-dimethylsilylene)(2,1'-diisopropylsilylene) (indenyl)  
 (3-trimethylsilylmethylindenyl) zirconium dichloride,  
 and (1,2'-diisopropylsilylene)(2,1'-diisopropylsilylene) (indenyl)  
 (3-trimethylsilylmethylindenyl) zirconium dichloride, and  
 compounds obtained by replacing zirconium of the above-described  
 compounds with titanium or hafnium, though not limited thereto.  
 In addition, similar compounds containing metal elements belonging to  
 the other Groups or lanthanoid series may also be used in the present  
 invention.

In the above-described compounds, the (1,1'-) (2,2'-) substituted  
 compounds may be replaced with (1,2'-) (2,1'-) substituted compounds,  
 and the (1,2'-) (2,1'-) substituted compounds may be replaced with  
 (1,1'-) (2,2'-) substituted compounds.

[0021]

Examples of the (B) organoboron compounds include  
 coordination complex compounds composed of an anion and a cation  
 containing a plurality of groups bonded to a metal element or Lewis  
 acids.

As the coordination complex compounds composed of an anion and a  
 cation containing a plurality of groups bonded to a metal element,  
 various compounds can be used. Suitable examples of these  
 coordination complex compounds include those compounds represented  
 by the following general formulae (17) and (18):



in the formulae (17) and (18),  $L^2$  represents  $M^4$ ,  $R^3 R^4 M^5$  or  $R^5_3 C$  as

defined later,  $L^1$  represents a Lewis base;  $M^2$  and  $M^3$  are respectively a boron atom;  $M^4$  is a metal selected from the group consisting of elements belonging to Group 1 and Groups 8 to 10 of the Periodic Table;  $M^5$  is a metal selected from the group consisting of elements belonging to Groups 8 to 10 of the Periodic Table;  $X^2$  to  $X^n$  are respectively a hydrogen atom, dialkylamino, alkoxy, aryloxy, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkylaryl group, an arylalkyl group, a substituted alkyl group, an organometalloid group or a halogen atom;  $R^3$  and  $R^4$  are respectively cyclopentadienyl, substituted cyclopentadienyl, indenyl or fluorenyl;  $R^5$  is an alkyl group;  $m$  represents a valence of  $M^2$  or  $M^3$  and is an integer of 1 to 7;  $n$  is an integer of 2 to 8;  $p$  represents an ionic valence of  $L^1 - H$  or  $L^2$  and is an integer of 1 to 7;  $q$  is an integer of 1 or more;  $l$  is a number of  $q \times p / (n - m)$ .

[0022]

$M^2$  and  $M^3$  are respectively a boron atom, and  $M^4$  is a metal selected from the group consisting of elements belonging to Group 1 and Groups 8 to 12 of the Periodic Table. Specific examples of the  $M^4$  include respective atoms such as Ag, Cu, Na and Li.  $M^5$  is a metal selected from the group consisting of elements belonging to Groups 8 to 10 of the Periodic Table. Specific examples of the  $M^5$  include atoms such as Fe, Co and Ni.

Specific examples of the  $X^2$  to  $X^n$  include dialkylamino groups such as dimethylamino and diethylamino; alkoxy groups such as methoxy, ethoxy and n-butoxy; aryloxy groups such as phenoxy, 2,6-dimethylphenoxy and naphthyloxy; alkyl groups having 1 to 20

carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, n-octyl and 2-ethylhexyl; aryl, alkylaryl or arylalkyl groups having 6 to 20 carbon atoms, such as phenyl, p-tolyl, benzyl, pentafluorophenyl, 3,5-di(trifluoromethyl)phenyl, 4-tert-butylphenyl, 2,6-dimethylphenyl, 3,5-dimethylphenyl, 2,4-dimethylphenyl and 1,2-dimethylphenyl; halogen atoms such as F, Cl, Br and I; and organometalloid groups such as pentamethyl antimony, trimethylsilyl, trimethylgermyl, diphenyl arsine, dicyclohexyl antimony and diphenyl boron.

Specific examples of the substituted cyclopentadienyl groups as  $R^3$  and  $R^4$  include methylcyclopentadienyl, butylcyclopentadienyl and pentamethylcyclopentadienyl.

[0023]

Specific examples of the anion containing a plurality of groups bonded to a metal element include  $B(C_6F_5)_4^-$ ,  $B(C_6HF_4)_4^-$ ,  $B(C_6H_2F_3)_4^-$ ,  $B(C_6H_3F_2)_4^-$ ,  $B(C_6H_4F)_4^-$ ,  $B(C_6(CF_3)F_4)_4^-$ ,  $B(C_6H_5)_4^-$ , and  $BF_4^-$ . Specific examples of the metal cation include  $Cp_2Fe^+$ ,  $(MeCp)_2Fe^+$ ,  $(tBuCp)_2Fe^+$ ,  $(Me_2Cp)_2Fe^+$ ,  $(Me_3Cp)_2Fe^+$ ,  $(Me_4Cp)_2Fe^+$ ,  $(Me_5Cp)_2Fe^+$ ,  $Ag^+$ ,  $Na^+$  and  $Li^+$ . Examples of the other cations include nitrogen-containing compounds such as pyridinium, 2,4-dinitro-N,N-diethyl anilinium, diphenyl ammonium, p-nitroanilinium, 2,5-dichloroaniline, p-nitro-N,N-dimethyl anilinium, quinolinium, N,N-dimethyl anilinium and N,N-diethyl anilinium; carbenium compounds such as triphenyl carbenium, tri(4-methylphenyl)carbenium and tri(4-methoxyphenyl)carbenium; alkyl phosphonium ions such as  $CH_3PH_3^+$ ,  $C_2H_5PH_3^+$ ,  $C_3H_7PH_3^+$ ,  $(CH_3)_2PH_2^+$ ,  $(C_2H_5)_2PH_2^+$ ,  $(C_3H_7)_2PH_2^+$ ,  $(CH_3)_3PH^+$ ,  $(C_2H_5)_3PH^+$ ,

$(\text{C}_3\text{H}_7)_3\text{PH}^+$ ,  $(\text{CF}_3)_3\text{PH}^+$ ,  $(\text{CH}_3)_4\text{P}^+$ ,  $(\text{C}_2\text{H}_5)_4\text{P}^+$  and  $(\text{C}_3\text{H}_7)_4\text{P}^+$ ; and aryl phosphonium ions such as  $\text{C}_6\text{H}_5\text{PH}_3^+$ ,  $(\text{C}_6\text{H}_5)_2\text{PH}_2^+$ ,  $(\text{C}_6\text{H}_5)_3\text{PH}^+$ ,  $(\text{C}_6\text{H}_5)_4\text{P}^+$ ,  $(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{PH}^+$ ,  $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{PH}_2^+$ ,  $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{PH}^+$  and  $(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2\text{P}^+$ .

In the present invention, used are coordination complex compounds composed of an optional combination of the above metal cations and anions.

[0024]

Specifically, of the compounds represented by the general formulae (17) and (18), following compounds are most suitably used.

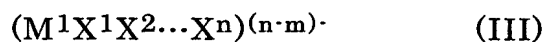
Examples of the compounds represented by the general formula (17) include triethyl ammonium tetraphenylborate, tri(n-butyl) ammonium tetraphenylborate, trimethyl ammonium tetraphenylborate, triethyl ammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl) ammonium tetrakis(pentafluorophenyl)borate, triethyl ammonium hexafluoroarsenate, pyridinium tetrakis(pentafluorophenyl)borate, pyrrolinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl anilinium tetrakis(pentafluorophenyl)borate, and methyldiphenyl ammonium tetrakis(pentafluorophenyl)borate.

Whereas, examples of the compounds represented by the general formula (18) include ferrocenium tetraphenylborate, dimethyl ferrocenium tetrakis(pentafluorophenyl)borate, ferrocenium tetrakis(pentafluorophenyl)borate, decamethyl ferrocenium tetrakis(pentafluorophenyl)borate,



acetyl ferrocenium tetrakis(pentafluorophenyl)borate,  
 formyl ferrocenium tetrakis(pentafluorophenyl)borate,  
 cyano-ferrocenium tetrakis(pentafluorophenyl)borate,  
 silver tetraphenylborate, silver tetrakis(pentafluorophenyl)borate,  
 trityl tetraphenylborate, trityl tetrakis(pentafluorophenyl)borate and,  
 silver tetrafluoroborate.

Suitable coordination complex compounds are those composed of a non-coordinated anion and a substituted triaryl carbenium. Examples of the non-coordinated anion include anions represented by the following general formula (III):



wherein  $M^1$  is a boron atom;  $X^1$  to  $X^n$  are respectively a hydrogen atom, dialkylamino, alkoxy, aryloxy, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms (including halogen-substituted aryl group), alkylaryl, arylalkyl, substituted alkyl, an organometalloid group or a halogen atom;  $m$  is a valence of  $M^1$ ; and  $n$  is an integer of 2 to 8.

[0025]

Further, compounds generally called "carborane" are also used as the non-coordinated anion.

Also, examples of the substituted triaryl carbenium include cations represented by the following general formula (IV):

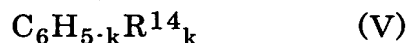


In the above general formula (IV),  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are respectively an aryl group such as phenyl, substituted phenyl, naphthyl and anthracenyl, and may be same or different from each other, and

at least one of them is substituted phenyl, naphthyl or anthracenyl.

[0026]

Examples of the substituted phenyl include groups represented by the following general formula (V):



In the above general formula (V),  $\text{R}^{14}$  is a hydrocarbyl having 1 to 10 carbon atoms, alkoxy, aryloxy, thioalkoxy, thioaryloxy, amino, amido, carboxyl or a halogen atom; and  $k$  is an integer of 1 to 5. When  $k$  is 2 or more, a plurality of the  $\text{R}^{14}$  groups may be same or different from each other.

[0027]

Specific examples of the non-coordinated anion represented by the general formula (III) include tetra(fluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(trifluoromethylphenyl)borate, tetra (toluyl)borate, tetra (xylyl)borate, (triphenyl, pentafluorophenyl)borate, [tris(pentafluorophenyl), phenyl]borate, and tridecahydride-7,8-dicarbaundecaborate.

[0028]

Specific examples of the substituted triaryl carbenium represented by the above general formula (IV) include tri(toluy)carbenium, tri(methoxyphenyl)carbenium, tri(chlorophenyl)carbenium, tri(fluorophenyl)carbenium, tri(xylyl)carbenium, [di(toluy), phenyl]carbenium, [di(methoxyphenyl), phenyl]carbenium, [di(chlorophenyl), phenyl]

carbenium, [toluyl, di(phenyl)]carbenium, [methoxyphenyl, di(phenyl)]carbenium, and [chlorophenyl, di(phenyl)]carbenium.

[0029]

In addition, as the organic boron compound as component (B) used in the catalyst of the present invention, there may also be used compounds represented by the following general formula:



wherein  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are respectively an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms. Namely, any of the boron compounds containing alkyl or aryl substituent groups bonded to boron may be used as the component (B) without any particular limitations.

The alkyl group herein may also include halogen-substituted alkyl groups, and the aryl group may also include halogen-substituted aryl groups and alkyl-substituted aryl groups.

[0030]

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  in the above general formula respectively represent an alkyl group having 1 to 20 carbon atoms or an aryl groups having 6 to 20 carbon atoms. Specific examples of the alkyl and aryl groups include alkyl groups such as methyl, ethyl, propyl, butyl, amyl, isoamyl, isobutyl, octyl and 2-ethylhexyl; and aryl groups such as phenyl, fluorophenyl, tolyl, xylyl and benzyl. Herein,  $\text{R}^1$  to  $\text{R}^3$  may be same or different from each other.

[0031]

Specific examples of the compounds represented by the above

general formula include triphenyl boron, tri(pentafluorophenyl)boron, tri(2,3,4,5-tetrafluorophenyl)boron, tri(2,4,5,6-tetrafluorophenyl)boron, tri(2,3,5,6-tetrafluorophenyl)boron, tri(2,4,6-trifluorophenyl)boron, tri(3,4,5-trifluorophenyl)boron, tri(2,3,4-trifluorophenyl)boron, tri(3,4,6-trifluorophenyl)boron, tri(2,3-difluorophenyl)boron, tri(2,6-difluorophenyl)boron, tri(3,5-difluorophenyl)boron, tri(2,5-difluorophenyl)boron, tri(2-fluorophenyl)boron, tri(3-fluorophenyl)boron, tri(4-fluorophenyl)boron, tri[3,5-di(trifluoromethyl)phenyl]boron, tri[ (4-fluoromethyl)phenyl]boron, diethyl boron, diethylbutyl boron, trimethyl boron, triethyl boron, tri(n-butyl) boron, tri(fluoromethyl) boron, tri(pentafluoroethyl) boron, tri(nonafluorobutyl) boron, tri(2,4,6-trifluorophenyl) boron, tri(3,5-difluorophenyl) boron, di(pentafluorophenyl) fluoroboron, diphenyl fluoroboron, di(pentafluorophenyl) chloroboron, dimethyl fluoroboron, diethyl fluoroboron, di(n-butyl) fluoroboron, (pentafluorophenyl) difluoroboron, phenyl fluoroboron, (pentafluorophenyl) dichloroboron, methyl difluoroboron, ethyl difluoroboron, and (n-butyl) difluoroboron.

Of these compounds, especially preferred is tri(pentafluorophenyl) boron.

The molar ratio of the component (A) to the component (B) used in the present invention is preferably 10:1 to 1:100 and more preferably 1:1 to 1:10. If the molar ratio of the component (A) to the component (B) is out of the above-specified range, the cost performance of the catalyst per unit mass of the obtained polymer is lowered and therefore

unpractical.

[0032]

The polymerization catalyst used in the production process of the present invention may further contain an organoaluminum compound as the component (C) in addition to the components (A) and (B).

As the organoaluminum compound (C), used are compounds represented by the general formula (VI):



wherein  $\text{R}^{16}$  is an alkyl group having 1 to 10 carbon atoms; J is a hydrogen atom, an alkoxy group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or a halogen atom; and v is an integer of 1 to 3.

Specific examples of the compounds represented by the above general formula (VI) include trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, triisobutyl aluminum, dimethyl aluminum chloride, diethyl aluminum chloride, methyl aluminum dichloride, ethyl aluminum dichloride, dimethyl aluminum fluoride, diisobutyl aluminum hydride, diethyl aluminum hydride and ethyl aluminum sesquichloride.

[0033]

These organoaluminum compounds may be used singly or in the form of a mixture of any two or more thereof.

In the production process of the present invention, the above described components (A), (B) and (C) may be preliminarily contacted with each other. The preliminary contact may be performed, for

example, by contacting the component (B) with the component (A), but is not particularly limited and may be conducted by any known method. The preliminary contact is effective to improve the catalytic activity, to reduce the amount of the component (B) as a co-catalyst, and as a result to reduce the costs required for the catalyst. Furthermore, when the components (A) and (B) are contacted with each other, in addition to the above effects, an effect of increasing a molecular weight of the obtained polymer can be obtained.

The preliminary contact temperature is usually in the range of  $-20$  to  $200^{\circ}\text{C}$ , preferably  $-10$  to  $150^{\circ}\text{C}$  and more preferably  $0$  to  $80^{\circ}\text{C}$ . The preliminary contact may also be conducted in the presence of an inert hydrocarbon solvent such as aliphatic hydrocarbons and aromatic hydrocarbons. Of these solvents, especially preferred are aliphatic hydrocarbons.

[0034]

The molar ratio of the catalyst component (A) to the catalyst component (C) is preferably in the range of from  $1:1$  to  $1:10,000$  and more preferably from  $1:5$  to  $1:2,500$ . When the catalyst component (C) is used, the catalyst can be enhanced in polymerization activity per unit quantity of transition metal used therein. However, if the amount of the catalyst component (C) is too large, the excess organoaluminum aluminum compounds are not used, and unfavorably remain in a large amount within the resulting polymer.

In the present invention, at least one of the catalyst components may be supported on a suitable carrier. The carrier to be used in the present invention is not particularly limited, and may be appropriately

selected from inorganic oxides, other inorganic materials and organic materials. Of these carriers, preferred are those made of inorganic oxides or other inorganic materials.

[0035]

The use of the supported catalyst enables production of polymers having an industrially useful high bulk density and an excellent particle size distribution.

The 1-butene-based polymer of the present invention can be produced by homopolymerizing 1-butene, or copolymerizing 1-butene with ethylene and/or an  $\alpha$ -olefin having 3 to 20 carbon atoms (except for 1-butene) in the presence of the above polymerization catalyst.

Examples of the  $\alpha$ -olefins include propylene having 3 to 20 carbon atoms, propylene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. In the present invention, these  $\alpha$ -olefins may be used singly or in the form of a mixture of any two or more thereof.

The polymerization methods usable in the present invention are not particularly limited, and include slurry polymerization, vapor-phase polymerization, bulk polymerization, solution polymerization, suspension polymerization and the like. Of these methods, preferred are slurry polymerization and vapor-phase polymerization.

[0036]

As to the polymerization conditions, the polymerization temperature is usually from  $-100$  to  $250^{\circ}\text{C}$ , preferably from  $-50$  to

200°C and more preferably from 0 to 130°C. The amounts of the reactants and the catalyst used may be controlled so that the molar ratio of the raw monomers to the above component (A) is preferably in the range of 1 to  $10^8$  and more preferably 100 to  $10^5$ . Further, the polymerization time is usually from 5 min to 10 h, and the reaction pressure is preferably from ordinary pressure to 20 MPa (gauge) and more preferably from ordinary pressure to 10 MPa (gauge).

[0037]

The molecular weight of the obtained polymer may be controlled by appropriately selecting kinds and amounts of respective catalyst components used, and polymerization temperature, or further by conducting the polymerization in the presence of hydrogen.

Examples of solvents to be used in the polymerization include aromatic hydrocarbons such as benzene, toluene, xylene and ethyl benzene; alicyclic hydrocarbons such as cyclopentane, cyclohexane and methyl cyclohexane; aliphatic hydrocarbons such as pentane, hexane, heptane and octane; and halogenated hydrocarbons such as chloroform and dichloromethane. These solvents may be used singly or in the form of a mixture of any two or more thereof. Also, the monomers such as  $\alpha$ -olefins may be used as the solvent. Meanwhile, the polymerization may also be performed in the absence of a solvent.

[0038]

Prior to the substantial polymerization, a preliminary polymerization may be conducted using the above polymerization catalyst. The preliminary polymerization may be conducted by contacting the solid catalyst component with, for example, a small



amount of olefins. The contact method is not particularly limited and may be any known method. The olefins to be used in the preliminary polymerization are not particularly limited, and the above-described olefins, e.g., ethylene,  $\alpha$ -olefins having 3 to 20 carbons or mixtures thereof can be used. It is advantageous that the olefins used in the preliminary polymerization are identical to those used in the subsequent substantial polymerization.

[0039]

The preliminary polymerization temperature is usually from  $-20$  to  $200^{\circ}\text{C}$ , preferably from  $-10$  to  $130^{\circ}\text{C}$  and more preferably from  $0$  to  $80^{\circ}\text{C}$ . The preliminary polymerization may be conducted in the presence of any suitable solvent such as aliphatic hydrocarbons, aromatic hydrocarbons and other monomers. Of these solvents, preferred are aliphatic hydrocarbons. The preliminary polymerization may be conducted in the absence of a solvent.

The preliminary polymerization conditions may be suitably controlled such that the product of the preliminary polymerization has an intrinsic viscosity  $[\eta]$  of  $0.2$  dL/g or higher and preferably  $0.5$  dL/g or higher as measured at  $135^{\circ}\text{C}$  in decalin, and the yield of the preliminary polymerization product is  $1$  to  $10,000$  g and preferably  $10$  to  $1,000$  g per one millimole of the transition metal contained in the catalyst.

[0040]

## [2] 1-Butene-Based Polymer

The 1-butene-based polymer according to the present invention satisfies the following requirements (1) to (3).

(1) an intrinsic viscosity  $[\eta]$  measured in a tetralin solvent at 135°C is 0.01 to 0.5 dL/g;

(2) a crystalline resin having a melting point ( $T_m - D$ ) is 0 to 100°C, the melting point being defined as a top of a peak observed on a highest-temperature side in a melting endothermic curve obtained by a differential scanning calorimeter (DSC) when a sample is held in a nitrogen atmosphere at 10°C for 5 min and then heated at a temperature rise rate of 10°C/min; and

(3) a stereoregularity index  $\{(mmmm)/(mmrr + rmmr)\}$  is 20 or lower.

[0041]

The 1-butene-based polymer according to the present invention has an intrinsic viscosity  $[\eta]$  of 0.01 to 0.5 dL/g as measured in a tetralin solvent at 135°C. The intrinsic viscosity  $[\eta]$  is preferably 0.1 to 0.5 dL/g. If the intrinsic viscosity  $[\eta]$  is less than 0.01 dL/g, the physical property (strength) of the resultant polymer tends to be lowered. If the intrinsic viscosity  $[\eta]$  exceeds 0.5 dL/g, the fluidity of the resultant polymer tends to be lowered.

The 1-butene-based polymer according to the present invention must be a crystalline resin having a melting point ( $T_m - D$ ) of 0 to 100°C, preferably 0 to 80°C as measured by differential scanning calorimeter (DSC) in view of a good softness thereof. The melting point ( $T_m - D$ ) is determined by the DSC measurement. That is, using a differential scanning calorimeter ("DSC-7" manufactured by Perkin Elmer Corp.), 10 mg of a sample is held in a nitrogen atmosphere at -10°C for 5 min, and then heated at a temperature rise rate of

10°C/minute to prepare a melting endothermic curve. The top of a peak observed on the highest temperature side in the melting endothermic curve is defined as the melting point ( $T_m - D$ ).

The crystalline resin used in the present invention means a resin which the measurable melting point ( $T_m - D$ ).

[0042]

In the present invention, the mesopentad fraction (mmmm) and the abnormal insertion content (1,4-insertion fraction) is determined according to the method reported and proposed in Asakura et al., "Polymer Journal", 16, 717 (1984), J. Randall et al., "Macromol. Chem. Phys.", C29, 201(1989), and V. Busico et al., "Macromol. Chem. Phys.", 198, 1257(1997).

More specifically, the mesopentad fraction and the abnormal insertion content in the molecule of poly(1-butene) are determined by measuring signals attributed to methylene and methine groups using  $^{13}\text{C}$  nuclear magnetic resonance spectrum.

The  $^{13}\text{C}$  nuclear magnetic resonance spectrum measurement is carried out using the following apparatus under the following conditions.

Apparatus:  $^{13}\text{C}$ -NMR spectrometer "JNM-EX400 Model" manufactured by JEOL Ltd.;

Method: proton complete decoupling method;

Sample concentration: 230 mg/mL;

Solvent: mixed solvent of 1,2,4-trichlorobenzene and heavy benzene (volume ratio: 90:10);

Measuring temperature: 130°C;

Pulse width: 45°;

Pulse repetition period: 4 s; and

Cumulative frequency: 10,000 times

In the present invention, the stereoregularity index  $\{(mmmm)/(mmrr + rmmr)\}$  is calculated from values (mmmm), (mmmr) and (rmmr) measured by the above method.

[0043]

The 1-butene-based polymer according to the present invention has a stereoregularity index  $\{(mmmm)/(mmrr + rmmr)\}$  of 30 or lower, preferably 20 or lower and more preferably 15 or lower.

If the stereoregularity index exceeds 30, the resultant polymer tends to be lowered in flexibility and fabricability. Here, the mesopentad fraction (mmmm) is preferably 20 to 90%, more preferably 40 to 85% and most preferably 60 to 80%. If the mesopentad fraction is less than 20%, the resultant molded article tends to exhibit stickiness on its surface or has a low transparency.

On the other hand, if the mesopentad fraction exceeds 90%, the resultant polymer tends to be lowered in flexibility and fabricability.

The 1-butene-based polymer according to the present invention has, in addition to the above requirements, a molecular weight distribution (Mw/Mn) of preferably 4 or lower, more preferably 3.5 or lower and still more preferably 3.0 or lower as measured by GPC. If the molecular weight distribution (Mw/Mn) exceeds 4, the resultant polymer tends to suffer from occurrence of stickiness.

The 1-butene-based polymer according to the present invention has, in addition to the above requirements, a weight-average molecular weight (Mw) of preferably 10,000 to 100,000 as measured by GPC. If the weight-average molecular weight (Mw) is less than 10,000, the resultant polymer tends to be lowered in physical properties (strength). In addition, if the weight-average molecular weight (Mw) exceeds 100,000, the resultant polymer tends to be lowered in fluidity, resulting in poor processability.

[0044]

Meanwhile, the above Mw/Mn is calculated from the weight-average molecular weight Mw and number-average molecular weight Mn in terms of polystyrene which are measured by GPC using the following apparatus and conditions:

GPC measuring apparatus

Column: TOSO GMHHR-H(S)HT

Detector: RI Detector "WATERS 150C" for liquid  
chromatogram

Measuring conditions:

Solvent: 1,2,4-trichlorobenzene

Measuring temperature: 145°C

Flow rate: 1.0 mL/min

Sample concentration: 2.2 mg/mL

Amount charged: 160 µL

Calibration curve: Universal Calibration

Analytic program: HT-GPC (Ver. 1.0)

[0045]

The 1-butene-based polymer according to the present invention preferably contains 1,4-insertion portions in an amount of 5% or lower. If the content of the 1,4-insertion portions exceeds 5%, the resultant polymer has a broad composition distribution, resulting in adverse influences on physical properties thereof.

The 1-butene-based polymer according to the present invention has a tensile modulus of preferably 500 MPa or lower and more preferably 300 MPa or lower as measured in a tensile test according to JIS K-7113. If the tensile modulus exceeds 500 MPa, the resultant polymer may fail to show a sufficient softness.

[0046]

When the 1-butene-based polymer of the present invention is in the form of a copolymer, the copolymer is preferably a random copolymer. In addition, the content of structural units derived from 1-butene in the copolymer is preferably 50 mol% or higher and more preferably 70 mol% or higher. If the content of structural units derived from 1-butene in the copolymer is less than 50 mol%, the resultant copolymer tends to be lowered in fabricability.

When the 1-butene-based polymer of the present invention is in the form of a copolymer, the copolymer has a randomness index of 1 or less as determined from  $\alpha$ -olefin chains according to the follow formula:

$$R = 4[\alpha\alpha][BB]/[\alpha B]^2$$

wherein  $[\alpha\alpha]$  represents an  $\alpha$ -olefin chain fraction;  $[BB]$  represents a butene chain fraction; and  $[\alpha B]$  represents an  $\alpha$ -olefin-butene chain fraction.

The randomness index R is an index representing a degree of

random copolymerization of the copolymer. The smaller the randomness index  $R$ , the higher the isolation of the  $\alpha$ -olefin (comonomer) becomes and the more uniform the composition thereof becomes.  $R$  is preferably 0.5 or lower and more preferably 0.2 or lower. When  $R$  is 0, no  $\alpha\alpha$  chains are present, and the  $\alpha$ -olefin chain is completely composed of an isolated chain solely.

When the 1-butene-based polymer is in the form of a propylene/butene copolymer, the butene content and  $R$  thereof are determined as follows.

Specifically, the butene content and  $R$  are calculated from  $^{13}\text{C}$ -NMR spectrum measured using an NMR apparatus "JNM-EX400 Model" available from JEOL Ltd., under the following conditions.

[0047]

Sample concentration: 220 mg/3 mL of NMR solution

NMR solution: 1,2,4-trichlorobenzene/benzene- $\text{d}_6$  (90/10 vol%)

Measuring temperature: 130°C

Pulse width: 45°

Pulse repetition period: 10 s

Cumulative frequency: 4,000 times

Under the above conditions, signals attributed to  $\text{S}\alpha\alpha$  carbon in  $^{13}\text{C}$ -NMR spectrum for PP, PB and BB chains are measured by the method proposed in J. C. Randall, "Macromolecules", 1978, 11, 592, to determine PP, PB and BB diad chain fractions in the molecular chain of the copolymer. From the respective diad chain fractions thus obtained, the butene content and the randomness index  $R$  are calculated

according to the following formulae:

[0048]

$$\text{Butene Content (mol\%)} = [\text{BB}] + [\text{PB}]/2$$

$$\text{Randomness Index } R = 4[\text{PP}][\text{BB}]/[\text{PB}]^2$$

wherein [PP] represents a propylene chain fraction; [BB] represents a butene chain fraction; and [PB] represents a propylene-butene chain fraction.

When the 1-butene-based polymer is in the form of an octene/butene copolymer, the butene content and R thereof are determined as follows.

Specifically, the butene content and R are calculated from  $^{13}\text{C}$ -NMR spectrum measured using an NMR apparatus "JNM-EX400 Model" available from JEOL Ltd., under the following conditions.

[0049]

Sample concentration: 220 mg/3 mL of NMR solution

NMR solution: 1,2,4-trichlorobenzene/benzene- $d_6$  (90/10 vol%)

Measuring temperature: 130°C

Pulse width: 45°

Pulse repetition period: 10 s

Cumulative frequency: 4,000 times

Under the above conditions, signals attributed to  $\text{S}\alpha\alpha$  carbon in  $^{13}\text{C}$ -NMR spectrum are measured to obtain OO, OB and BB diad chain fractions in the molecular chain of the copolymer from the peak intensity values derived from BB chain observed at 40.8 to 40.0 ppm, OB chain observed at 41.3 to 40.8 ppm and OO chain observed at 42.5 to



41.3 ppm. From the respective diad chain fractions (mol%) thus obtained, the butene content and randomness index R are calculated according to the following formulae:

[0050]

$$\text{Butene Content (mol\%)} = [\text{BB}] + [\text{OB}]/2$$

$$\text{Randomness Index R} = 4[\text{OO}][\text{BB}]/[\text{OB}]^2$$

wherein [OO] represents an octene chain fraction; [BB] represents a butene chain fraction; and [OB] represents an octene-butene chain fraction.

When the 1-butene-based polymer of the present invention is homopolymer, it can preferably be produced according to the production process (a) described above. When the 1-butene-based polymer of the present invention is a copolymer, the production process (a') described above is suitable to the production thereof.

[0051]

### [3] 1-Butene-Based Resin Modifier

The 1-butene-based resin modifier of the present invention is made of the 1-butene-based polymer described above. The 1-butene-based resin modifier of the present invention can exhibit a low melting point, a good softness and a less stickiness, and can provide a molded article that are excellent in compatibility with polyolefin resins.

Specifically, the 1-butene-based resin modifier of the present invention is composed of the specific 1-butene-based homopolymer and the specific 1-buten-based copolymer and especially includes a slight amount of crystalline portions in poly-1-butene chain moieties thereof.

As a result, the 1-butene-based resin modifier of the present invention exhibits a less stickiness and is excellent in compatibility as compared with conventional modifiers such as soft polyolefin resins. Further, the 1-butene-based resin modifier of the present invention is excellent in compatibility with polyolefin-based resins, in particular, polypropylene-based resins.

As a result, the 1-butene-based resin modifier of the present invention is prevented from undergoing fall in surface properties (stickiness), and exhibits a high transparency as compared with conventional modifiers such as ethylene-based rubbers.

In view of the above advantageous properties, the 1-butene-based resin modifier of the present invention can suitably be used as a modifier for improving properties such as flexibility and transparency. Furthermore, the 1-butene-based resin modifier of the present invention may also suitably be used as a modifier for improving heat sealability and hot tackiness.

[0052]

The present invention will be described in more detail by reference to the following examples. However, the following examples are not intended to limit the invention thereto.

First, methods for evaluating resin properties of the 1-butene-based polymers obtained by the production process of the present invention are explained.

(1) Measurement for Mesopentad Fraction, Abnormal Insertion Content and Stereoregularity Index

Measured by the methods described in the present specification.

(2) Measurement for Comonomer Content

Measured by the method described in the present specification.

(3) Measurement for Intrinsic Viscosity  $[\eta]$

Measured at 135°C in a tetralin solvent using an automatic viscometer "VMR-053 Model" available from RIGO Co., Ltd.

(4) Measurement for Weight-Average Molecular Weight ( $M_w$ ) and Molecular Weight Distribution ( $M_w/M_n$ )

Measured by the method described in the present specification.

(5) DSC Measurement (Measurement for Melting Point:  $T_m - D$ )

Measured by the method described in the present specification. Specifically, using a differential scanning calorimeter "DSC-7" manufactured by PerkinElmer, Inc., 10 mg of a sample was held in a nitrogen atmosphere at  $-10^\circ\text{C}$  for 5 min, and then heated at a temperature rise rate of  $10^\circ\text{C}/\text{min}$  to prepare a melting endothermic curve thereof. The melting point ( $T_m - D$ ) was defined as a top of a peak observed on the highest-temperature side in the thus prepared melting endothermic curve. The melting endotherm as determined by the above measurement was expressed by  $\Delta H - D$ .

(6) Measurement for Tensile Modulus and Tensile Elongation at Break

The polymer was press-molded into a specimen, which was subjected to a tensile test according to JIS K-7113 under the following condition.

Cross-head speed: 50 mm/min

[0053]

EXAMPLE 1

<1>Preparation of Catalyst

(1) Production of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl) zirconium dichloride

In a Schlenk bottle, 3.0 g (6.97 mM) of a lithium salt of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(indene) was dissolved in 50 mL of THF (tetrahydrofuran), and cooled to  $-78^{\circ}\text{C}$ . Then, 2.1 mL (14.2 mM) of iodomethyl trimethylsilane was slowly dropped to the solution, and the mixture was stirred at room temperature for 12 h.

From the resultant reaction solution, the solvent was distilled away, then 50 mL of ether was added to the residue, and the reaction solution was washed with a saturated ammonium chloride solution. An organic phase separated from the solution was dried, and the solvent was removed therefrom, thereby obtained was 3.04 g (5.88 mM) of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindene) (yield:84%).

Next, a Schlenk bottle was charged with 3.04 g (5.88 mM) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindene) obtained above and 50 mL of ether under a nitrogen flow. After the contents of the bottle were cooled to  $-78^{\circ}\text{C}$ , 7.6 mL (1.7 mM) of a hexane solution (1.54M) of n-BuLi was dropped thereto. The resultant mixture was heated to room temperature, and then stirred at room temperature for 12 h, and the ether was distilled away from the reaction mixture.

The resultant solid was washed with 40 mL of hexane to obtain 3.06 g (5.07 mM) of a lithium salt in the form of an ether adduct (yield: 73%).

The results of  $^1\text{H}$ -NMR (90 MHz,  $\text{THF-d}_8$ ) measurement of the product were as follows:

$\delta$ : 0.04 (s, 18H, trimethylsilyl); 0.48 (s, 12H, dimethylsilylene); 1.10 (t, 6H, methyl); 2.59 (s, 4H, methylene); 3.38 (q, 4H, methylene); 6.2-7.7 (m, 8H, Ar-H)

The lithium salt obtained above was dissolved in 50 mL of toluene under a nitrogen flow. After the resultant solution was cooled to  $-78^\circ\text{C}$ , a suspension prepared by dispersing 1.2 g (5.1 mM) of zirconium tetrachloride in 20 mL of toluene which was previously cooled to  $-78^\circ\text{C}$ , was dropped into the solution. After completion of the dropping, the resultant mixture was stirred at room temperature for 6 h. From the resultant reaction solution, the solvent was distilled away. The distillation residue was recrystallized with dichloromethane, thereby 0.9 g (1.33 mM) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl) zirconium dichloride was obtained (yield: 26%).

The results of  $^1\text{H}$ -NMR (90 MHz,  $\text{CDCl}_3$ ) measurement of the product were as follows:

$\delta$ : 0.0 (s, 18H, trimethylsilyl); 1.02, 1.12 (s, 12H, dimethylsilylene); 2.51 (dd, 4H, methylene); 7.1-7.6 (m, 8H, Ar-H)

[0054]

## <2> Polymerization

A one liter autoclave previously heat-dried was charged with 200 mL of heptane, 200 mL of 1-butene and 0.5 mM of triisobutyl aluminum, and then hydrogen was introduced into the autoclave until reaching 0.2

MPa. After the contents of the autoclave was heated to 65°C while stirring, 0.8  $\mu$ M of triphenyl carbenium tetrakis(pentafluorophenyl) borate and 0.2  $\mu$ M of (1,2'-dimethylsilylene)-(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride were added thereto, and the polymerization was conducted for 5 min. After completion of the polymerization reaction, the resultant reaction product was dried under reduced pressure to obtain 13 g of a 1-butene polymer.

The resin properties and physical properties of the 1-butene polymer thus obtained were evaluated by the above-described methods. The results are shown in Table 1.

[0055]

## EXAMPLE 2

### <1> Preparation of Catalyst

In the same manner as in Example 1, (1,2'-dimethylsilylene)-(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride was produced.

### <2> Polymerization

A one liter autoclave previously heat-dried was charged with 200 mL of heptane, 200 mL of 1-butene and 0.5 mM of triisobutyl aluminum, and then hydrogen was introduced into the autoclave until reaching 0.3 MPa. After the contents of the autoclave was heated to 65°C while stirring, propylene was further continuously introduced into the autoclave until a total pressure thereof reached 0.8 MPa. Then, 0.8  $\mu$ M of triphenyl carbenium tetrakis(pentafluorophenyl) borate and 0.2  $\mu$ M of (1,2'-dimethylsilylene)

(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride were added thereto, and the polymerization was conducted for 5 min. After completion of the polymerization reaction, the resultant reaction product was dried under reduced pressure to obtain 14 g of a 1-butene copolymer.

The resin properties and physical properties of the 1-butene copolymer thus obtained were evaluated by the above-described methods. The results are shown in Table 1.

[0056]

### EXAMPLE 3

#### <1> Preparation of Catalyst

In the same manner as in Example 1, (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride was produced.

#### <2> Polymerization

A one-liter autoclave previously heat-dried was charged with 200 mL of heptane, 200 mL of 1-butene, 10 mL of 1-octene and 0.5 mM of triisobutyl aluminum, and then hydrogen was introduced into the autoclave until reaching 0.3 MPa. After the contents of the autoclave was heated to 65°C while stirring, 2  $\mu$ M of triphenyl carbenium tetrakis(penta-fluorophenyl borate and 0.5  $\mu$ M of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride were added thereto, and the polymerization was conducted for 5 min. After completion of the polymerization reaction, the resultant reaction product was dried under reduced pressure to obtain 13 g of a 1-butene copolymer.

The resin properties and physical properties of the 1-butene copolymer thus obtained were evaluated by the above-described methods. The results are shown in Table 1.

[0057]

#### COMPARATIVE EXAMPLE 1

The same procedure as in EXAMPLE 1 was repeated except for replacing 0.8  $\mu$ M of triphenyl carbenium tetrakis(pentafluorophenyl)borate with 0.25 mM of methyl aluminoxane, and using (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylindenyl)zirconium dichloride in an amount of 0.25  $\mu$ M. The polymerization reaction was conducted for 30 min, and the resultant reaction product was dried in the same manner as in EXAMPLE 1, thereby obtaining 10 g of a 1-butene polymer.

The resin properties and physical properties of the 1-butene copolymer thus obtained were evaluated by the above-described methods. The results are shown in Table 1.

Both EXAMPLE 1 and COMPARATIVE EXAMPLE 1 relate to the production of 1-butene polymers. However, in COMPARATIVE EXAMPLE 1, the polymers using methyl aluminoxane instead of the organoboron compound showed a large intrinsic viscosity  $[\eta]$  as 1.0, and a high fluidity was not obtained.

[0058]



[Table 1]

	Examples			Com. Ex.
	1	2	3	1
Mesopentad fraction (mmmm) (mol%)	71.2	-	-	72
Abnormal insertion content (1,4-insertion fraction) (mol%)	0	-	-	0
Kind of comonomer	-	propylene	1-octene	-
Comonomer content (mol%)	-	27	3	-
Stereoregularity index (mmmm/(mmrr + rmmr))	8	9	9	8
Intrinsic viscosity $[\eta]$ (dL/g)	0.4	0.4	0.4	1.0
Weight-average molecular weight $\times 10^4$ (Mw)	8	9	8	28
Molecular weight distribution (Mw/Mn)	2.0	2.0	2.0	2
Melting point ( $T_m - D$ ) ( $^{\circ}\text{C}$ )	67	41	46	65
Melting endotherm ( $\Delta H$ ) (J/g)	38	14	29	40
Tensile modulus (MPa)	270	60	105	200
Elongation at break (%)	120	650	510	470

[0059]

[Effect of the Invention]

According to the present invention, it is possible to produce a 1-butene-based polymer having a uniform composition, a well-controlled stereoregularity, a high fluidity and a high flexibility. The 1-butene-based resin modifier of the present invention can provide a molded article exhibiting a good softness, a less stickiness and an excellent compatibility with polyolefin resins.

[Name of Document]      ABSTRACT

[Abstract]

[Problem]

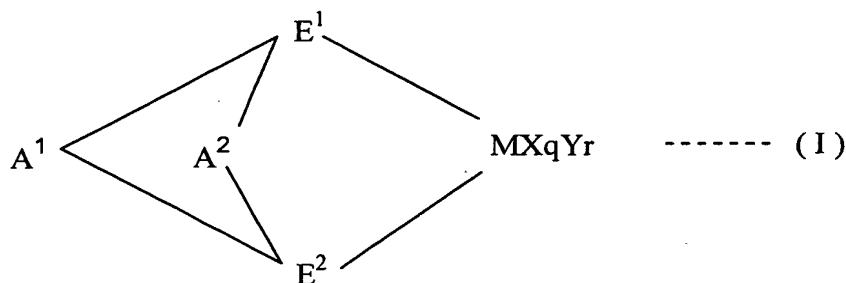
To provide a process for producing a high-fluidity 1-butene-based polymer.

[Means to Solve the Problem]

A process for producing a high-fluidity 1-butene-based polymer, that is, (a) a process for producing a high-fluidity 1-butene-based homopolymer, which comprises polymerizing 1-butene, and (a') a process for producing a high-fluidity 1-butene-based copolymer, which comprises copolymerizing 1-butene with ethylene and/or an  $\alpha$ -olefin having 3 to 20 carbon atoms (excluding 1-butene), in the presence of a polymerization catalyst comprising

(A) a transition metal compound represented by the following general formula (I):

[Chemical Formula 1]



wherein M is a metal element belonging to Groups 3 to 10 or lanthanoid of the Period Table;

$\text{E}^1$  and  $\text{E}^2$  are independently a ligand selected from the group consisting of substituted indenyl groups and the like, X is a ligand capable of forming a  $\sigma$ -bond, Y is a Lewis base,  $\text{A}^1$  and  $\text{A}^2$  are divalent

cross-linking groups capable of bonding the two ligands,  $q$  is an integer of 1 to 5 given by the formula:  $[(\text{valence of M}) - 2]$ ; and  $r$  is an integer of 0 to 3, and

(B) an organoboron compound.

[Selected Drawing]    None